Chapter 5

Synthesis and Structure of 1,2,6-Trisila-5-germabenzvalene and Its Isomerization to 1,2,5-Trisila-6-germabenzvalene

Summary

1,2,5,6-Tetrakis[di-*tert*-butyl(methyl)silyl]-4-phenyl-1,2,6-trisila-5-germabenzvalene was obtained by the reductive dehalogenation of 1,2,3,4-tetrakis[di-*tert*-butyl(methyl)silyl]-5-phenyl-1,2,3-trisila-4-germabicyclo[2.2.0]hex-5-ene **10** with KC_8. The molecular structure of **17** was determined by spectroscopic method as well as X-ray single crystal analysis. Interestingly, 1,2,6-trisila-5-germabenzvalene **17** thermally and photochemically isomerizes to 1,2,5-trisila-6-germabenzvalene **20** *via* a skeletal rearrangement.

Introduction

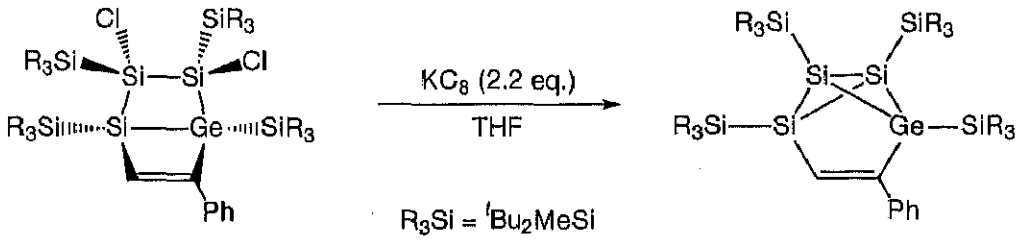
Although the chemistry of valence isomers of benzene such as Dewar-benzene and benzvalene has been well-studied,[1] the heavy analogue of those compounds containing heavier Group 14 elements (Si and Ge) are less-studied in spite of explosive development of research on synthesis of stable silabenzene and related compounds.[2-7] The photochemical isomerization of the isolable silabenzene derivative bearing a bulky substituent to the corresponding 2-silabenzvalene derivative was reported by Tokitoh et al. in 2000,[2b] and also a stable 1,4-disilabenzvalene[8] and Dewar-1,4-disilabenzene[9] derivatives were reported by Ando et al. in 1997 and 2000, respectively. Quite recently, Tokitoh et al. reported photochemical isomerization of 9-silaanthracene to 9,10-Dewar-9-silaanthracene.[10] There are no examples of benzene and its valence isomers containing three or more over silicon and germanium atoms are known except for the observation of Dewar-hexasilabenzene by using UV-Vis spectrum.[11]

As described in chapter 1, the author successfully synthesized *trans*-3,4-dichloro-5-phenyl-1,2,3,4-tetrakis[di-*tert*-butyl(methyl)silyl]-1,2,3-trisila-4-germabicyclo[2.2.0]hex-5-ene **10** by the regioselective cycloaddition of phenylacetylene to the corresponding trisilagermacyclobutene derivative **9** with an endocyclic Si=Ge double bond. Compound **10** has two chlorine atoms at bridged silicon atoms prompt the author easy to introduce a Si=Si double bond by reductive dehalogenation to produce the heavy analogue of Dewar-benzene derivative. However, the reductive dehalogenation of **10** did not afford the corresponding Dewar-trisilagermabenzene derivative, but 1,2,6-trisila-5-germabenzvalene **17**. In this chapter, synthesis and characterization of the first 1,2,6-trisila-5-germabenzvalene derivative are described. The thermal and photochemical isomerization of **17** to 1,2,5-trisila-6-germabenzvalene **20** is also discussed.

Results and Discussion

Synthesis and Structure of 1,2,6-trisila-5-germabenzvalene

The crystals of **10** and two molar amount of potassium graphite (KC_8) were placed in a reaction vessel, and stirred in oxygen-free, dry THF for 2 hour at room temperature. The resulting potassium salt and graphite were removed by filtration after exchange of solvent to hexane. The reaction mixture was recrystallized from hexane at -30 °C to afford pale-yellow crystals of 4-phenyl-1,2,5,6-tetrakis[di-*tert*-butyl(methyl)silyl]-1,2,6-trisila-5-germabenzvalene **17** in 31% yield (scheme 5-1).



10 **17**

Scheme 5–1

The structure of **17** has been determined by MS and ^1H, ^{13}C, ^{29}Si NMR spectroscopy as well as X-ray crystallography. The ^1H NMR in benzene-d_6 showed one olefinic proton at 6.93 ppm, as well as peaks indicating the presence of three kinds of $^tBu_2MeSi$ groups, and one phenyl group. The ^{29}Si NMR spectrum in benzene-d_6 showed five signals at $\delta = -102.2$ (2 Si), –94.8, 17.1, 25.7, and 29.6. The signal at $\delta = -102.2$ can be assigned to skeletal silicon atoms at 1,6-positions and the signal at $\delta = -94.8$ can be assigned to the silicon atom at 2-position in the 1,2,6-trisila-5-germabenzvalene skeleton, respectively. Such a characteristic shielding chemical shifts for the skeletal silicon atoms are similar to silyl-substituted small ring systems containing silicon atoms such as cyclotrisilane derivatives.

The molecular structure of **17** was identified by X-ray analysis of a single crystal

obtained by recrystallization from hexane, and an ORTEP drawing of the molecular structure of **17** is given in Figure 5-1. The skeletal Si–Si bond lengths of Si1–Si2, Si1–Si3, and Si2–Si3 are 2.3590(7), 2.3435(7), and 2.3429(7) Å, respectively, which lies in the normal Si–Si single bond region (2.33 – 2.37 Å). The Ge-Si single bond lengths in the tricyclic skeleton (Ge1–Si1; 2.4076(7), Ge1–Si3; 2.4309(7) Å) are also usual value.

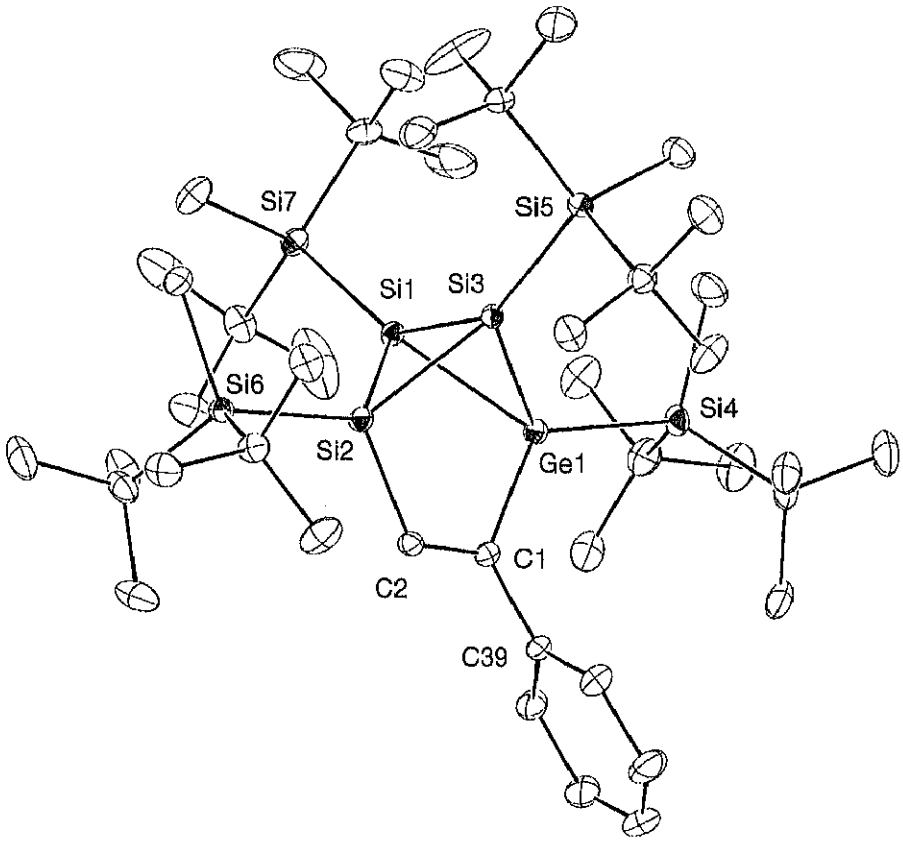
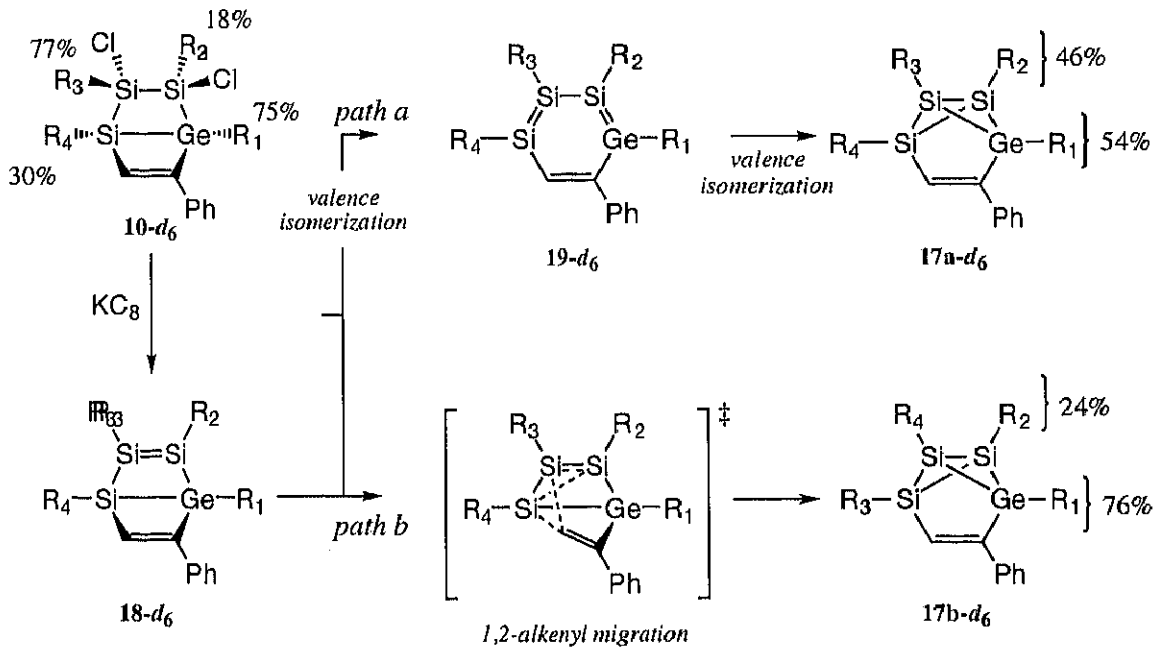


Figure 5–1. ORTEP drawing of **17** (hydrogen atoms are omitted for clarity).

The Formation Mechanism of 1,2,6-Trisila-5-germabenzvelene

It is likely that the formation of 1,2,6-trisila-5-germabenzvelene derivative **17** proceeds via *pathway a* or *pathway b* (Scheme 5-2): a valence isomerization of Dewar-1,2,3-trisila-4-germabenzene derivative **18**, which can be produced by the reductive dehalogenation of **10**, to 1,2,6-trisila-5-germabenzvelene **17** *via* 1,2,3-trisila-4-germabenzene **19** (*path a*); or a one-step isomerization involving 1,2-migration of alkenyl group

bounded to the bridgehead silicon atom in the Dewar-1,2,3-trisila-4-germabenzene skeleton to sp^2 silicon atom (*path b*). To differentiate between these possibilities, the reduction of the deuterium-labeled 1,2,3-trisila-4-germabicyclo[2.2.0]hex-5-ene derivative (**10**-d_6),[12] which was prepared by the reaction of deuterium-labeled cyclotrisilene **3**-d_6 with $GeCl_2$ dioxane and phenylacetylene, has been performed. If the isomerization occurs via *path a*, the ratio of the intensities of the methyl groups on the 1,6-position to those on the 2,5-positions would be 46 : 54 in the ^1H NMR spectrum.[13] On the other hand, in the case of isomerization via 1,2-alkenyl migration, path b, the ratio of the intensities of the methyl groups on the 1,6-position to those on the 2,5-positions would be 24 : 76. In fact, the reduction of **10**-d_6 under the same conditions as shown in Scheme 5-1 produced **17b**-d_6, the ratio of signals at 0.31 and 0.43 ppm assigned to methyl groups was 24 : 76. This result indicates that the formation of **17** occurs *via* 1,2-alkenyl migration of trisilagermacyclobutene moiety in the Dewar-1,2,3-trisila-4-germabenzene skeleton, rather than *via* a valence isomerization through a trisilagermabenzene derivative as an intermediate.



Scheme 5–2

To have better understanding of the isomerization pathway from Dewar-1,2,3-trisila-4-germabenzene **18** to 1,2,6-trisila-5-germabenzvelene **17** (*path a* or *path b*), theoretical calculations on valence isomers of the parent trisilagermabenzene system (**17-H** to **19-H**) were carried out at the B3LYP/6-31G(d) level, and all valence isomers **17-H** - **19-H** were found as energy minimum geometries. As shown in Figure 5-2, at the B3LYP/6-31G(d) level of theory, the isomerization of **18-H** to **19-H** is computed to be exothermic by 3.2 kcal/mol and to require passage over a TS 27.5 kcal/mol higher in energy than the reactant. The isomerization of **19-H** to **17-H** is also exothermic by 5.4 kcal/mol and to require passage over a TS 31.1 kcal/mol higher in energy than **19-H**. On the other hand, the isomerization of **18-H** to **19-H** via 1,2-alkenyl migration is computed to be exothermic by 8.6 kcal/mol and to require passage over a barrier of 22.6 kcal/mol. Thus, as illustrated graphically in Figure 5-2, the theoretical calculation shows that the isomerization of **18-H** to **17-H** through 1,2-alkenyl migration (path b) is more favored energetically than *via* a valence isomerization through a trisilagermabenzene derivative as a intermediate, which is consistent with present experimental result.

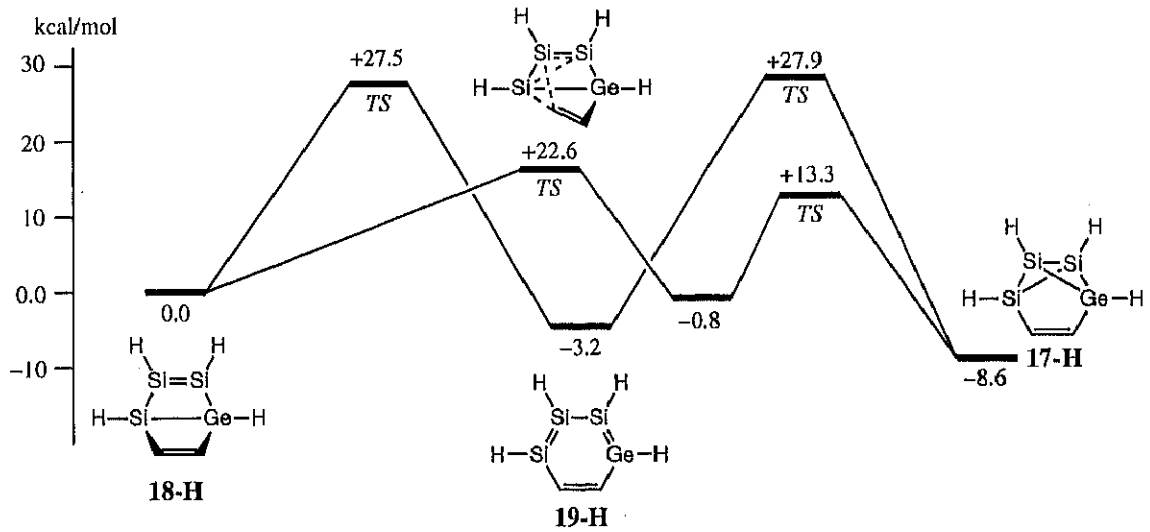
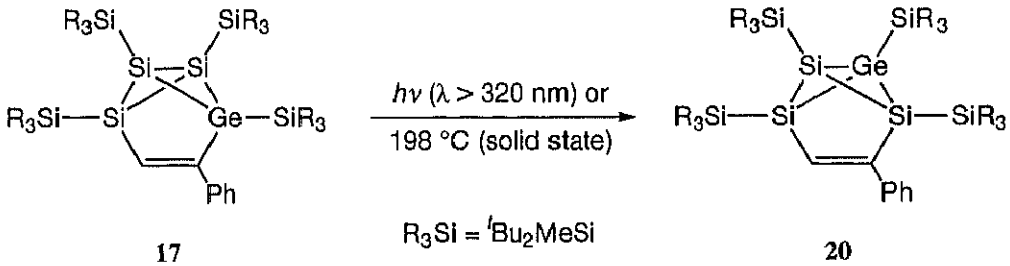


Figure 5–2. Calculated energy serface for isomerization of $Si_3GeC_2H_6$ isomers (computed at B3LYP/6-31G(d) level of theory).

Photochemical and Thermal Reaction of 1,2,6-Trisila-5-germabenzvalene 17

It is well-known that benzvalene derivatives in all carbon system thermally and photochemically isomerized to benzene.[1] Consequently, the photochemical and thermal reaction of 1,2,6-trisila-5-germabenzvalene derivative **17** were investigated.

Upon irradiation a benzene-d_6 solution of **17** in a sealed NMR tube with a high pressure Hg lamp (> 320 nm), **17** was disappeared with in 6 hour. After removal the solvent, the reaction mixture was recrystallized from hexane to afford 1,2,5,6-tetrakis[di-*tert*-butyl(methyl)silyl]-3-phenyl-1,2,5-trisila-6-germabenzvalene **20** in an almost quantitative yield (Scheme 5-3). The isomerization of **17** to **20** was also proceeded under thermal condition such as heating of **17** at 198 °C without solvent.



17 **20**

Scheme 5–3

The structure of **20** was determined by MS spectrometry as well as ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. In contrast to **17**, seven signals were observed at δ = –104.1, –89.4, –88.1, 16.7, 17.4, 25.9, and 37.2 in the ^{29}Si NMR spectrum. The signal at δ = –104.1 can be assigned to skeletal silicon atom at 1-positions and the signals at δ = –89.4, and –88.1 can be assigned to the silicon atom at 2,5-positions in the 1,2,5-trisila-6-germabenzvalene skeleton, respectively. Theoretical calculations on model compounds of the parent trisilagermabenzvalenes (**17-H** and **20-H**) showed that **20-H** is thermodynamically more stable by 7.0 kcal/mol relative to **17-H**. This difference in energy is probably due to the degree of ring strain at $GeSi_3$ bicyclic moiety.

Conclusions

1,2,6-Trisila-5-germabenzvalene derivative **17** was obtained by the reductive dehalogenation of 3,4-dichloro-1,2,3-trisila-4-germabicyclo[2.2.0]hex-5-ene derivative **10** with KC_8 in THF. Both deuterium-labeled experiment and theoretical calculations showed that formation of **17** occurs *via* 1,2-alkenyl migration of Dewar-1,2,3-trisila-4-germabenzene which was initially formed by reduction of **10,** rather than *via* a valence isomerization through a trisilagermabenzene derivative as an intermediate. The author was also found that **17** was thermally and photochemically isomerized to 1,2,5-trisila-6-germabenzvalene derivative **20.**

Experimental Section

General procedure

All reactions involving air-sensitive compounds were carried out under argon atmosphere using high-vacuum line and standard Schlenk techniques and dry, oxygen-free solvents. NMR spectra were recorded on a Bruker AC-300FT NMR spectrometer (^{1}H NMR at 300.13 MHz; ^{13}C NMR at 75.47 MHz; ^{29}Si NMR at 59.63 MHz). Mass spectra were obtained on a JEOL JMS SX-102 instrument (EI, 70 eV). UV spectra were recorded on a Shimadzu UV-3150 UV-visible spectrophotometer in hexane. Elemental analyses were performed at the Analytical Centers of Tsukuba University (Tsukuba, Japan) and Tohoku University (Sendai, Japan).

Synthesis of 4-phenyl-1,2,5,6-Tetrakis[di-tert-butyl(methyl)silyl]-1,2,6-trisila-5-germabenzvalene 17

The crystals of **10** (60 mg, 0.0063 mmol) and potassium graphite (20 mg, 0.148 mmol) were placed in a reaction vessel with a magnetic stirrer. Then, degassing the tube, dry oxygen-free THF was introduced by vacuum transfer, and stirred for 2 h. After the solvent was removed in vacuo, degassed hexane was introduced, and the graphite and resulting potassium salt had been removed by filtration. The reaction mixture was recrystallized from hexane to afford pale-yellow crystals of **17** in 31% yield. mp 198 °C (dec.); ^{1}H NMR (C_6D_6, δ) 0.31 (s, 6 H), 0.43 (s, 36 H), 1.07 (s, 18 H), 1.24 (s, 18 H), 1.27 (s, 18 H), 1.29 (s, 18 H), 6.93 (s, 1 H), 6.94 (t, J = 7.3 Hz, 1 H), 7.03 (t, J = 7.3 Hz, 2 H) 7.11 (d, J = 7.3 Hz, 2 H); ^{13}C NMR (C_6D_6, δ) –5.5, –3.2, –2.4, 21.6, 21.7, 21.8, 30.3, 30.5, 30.6, 125.8, 127.5, 127.9, 148.2, 149.4, 179.2; ^{29}Si NMR (C_6D_6, δ) –102.2, –94.8, 17.1, 25.7, 29.6; MS m/z(%) 873 (M^+ - Me), 731 (M^+ - SiMe^{t}Bu$_2$), 73 (100); UV-Vis

(hexane) λ_{max}/nm (ε) 342 (4300), 302 (sh, 10500), 240 (65300).

Photolchemical Isomerization of 1,2,6-tri-sila-5-germabenzvalene 16

Upon irradiation a benzene-d_6 solution of **16** (20 mg, 0.023 mmol) in a sealed NMR tube with a high pressure Hg lamp (λ > 320 nm), **16** was disappeared within 6 hour. After removal the solvent, the reaction mixture was recrystallized from hexane to afford pale-yellow crystals of 3-phenyl-1,2,5,6-tetrakis[di-*tert*-butyl(methyl)silyl]-1,2,5-trisila-6-germa-benzvalene **20** in an almost quantitative yield. Pale-yellow crystals; mp 208 °C (dec.); ^{1}H NMR (C_6D_6, δ) 0.28 (s, 3 H), 0.30 (s, 3 H), 0.44 (s, 3 H), 0.47 (s, 3 H), 1.08 (s, 9 H), 1.11 (s, 9 H), 1.22 (s, 9 H), 1.24 (s, 9 H), 1.27 (s, 9 H), 1.29 (s, 9 H), 1.30 (s, 9 H), 1.31 (s, 9 H), 6.94 (t, J = 7.6 Hz, 1 H), 7.03 (t, J = 7.6 Hz, 2 H), 7.10 (d, J = 7.3 Hz, 2 H), 7.29 (s, 1 H); ^{13}C NMR (C_6D_6, δ) –5.6, –3.2, –2.8, –2.4, 21.17, 21.23, 21.6, 21.7, 21.8 (2 C), 22.4 (2 C) 125.8, 127.8, 128.0, 149.0, 159.3, 175.0; ^{29}Si NMR (C_6D_6, δ) –104.1,–89.4, –88.1, 16.7, 17.4, 25.9, 37.2; UV/Vis (hexane): λ_{max}/nm (ε) 342 (4300), 302 (sh, 10500), 240 (65300); Anal. Calcd for $C_{44}H_{90}GeSi_7$: C, 59.49; H, 10.21%. Found: C, 59.39; H, 10.01%.

Thermal reation of 1,2,6-trisila-5-germabenzvalene 17

Pale-yellow crystals of **17** (10 mg, 0.012 mmol) in a NMR tube was heated at 198 °C for 3 minutes ander argon atmosphere, the crystals of **17** was melted. After cooling to room temperature, dry benzene-d_6 was introduced by vacuum transfer and sealed the NMR tube. The formation of 1,2,5-trisila-6-germa-benzvalene derivative **20** was confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy.

Theoretical Calculation for Isomerization of 1,2,6-Trisila-5-germabenzvalene

All calculations were performed with the Gaussian 98 series of program[14]. All structures were optimized in the given symmetry at B3LYP/6-31G(d) level. Vibrational frequencies were calculated at the same level to determined the nature of the stationary points and transiton state as well as the zero-point energy correction.

X-ray Crystal Structure Determination of 17

A single crystal of **17** for X-ray diffraction was grown from a hexane solution. Diffraction data were collected at 120 K on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized Mo–Ka radiation (λ = 0.71070 Å). The structure was solved by the direct method and refined by the full-matrix least-squares method using SHELXL-97 program. Details of crystal data and structure refinement of are summarized in Table 5-1a. The final atomic parameters, the bond length, and the bond angles of **17** are listed in Table 5-1b and Table 5-1c, respectively.

Table 5-1a. Crystal data and structure refinement for **17**

Empirical formula	$C_{44}H_{90}GeSi_7$	
Formula weight	888.38	
Temperature	120 K	
Wavelength	0.71070 Å	
Crystal system, space group	Monoclinic, $P\ 2_1/c$	
Unit cell dimensions	a = 15.1630(4) Å b = 19.3050(3) Å c = 18.9250(5) Å	alpha = 90 deg. beta = 100.566(1) deg. gamma = 90 deg.
Volume	5445.8(2) Å^3	
Z, Calculated density	4, 1.084 Mg/m^3	
Absorption coefficient	0.743 mm^-1	
F(000)	1936	
Crystal size	0.30 x 0.25 x 0.25 mm	
Theta range for data collection	2.17 to 28.00 deg.	
Limiting indices	0<=h<=19, 0<=k<=25, -24<=l<=24	
Reflections collected / unique	13090 / 55206 [R(int) = 0.0410]	
Completeness to theta = 27.94	99.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13090 / 0 / 470	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0390, wR2 = 0.1063	
R indices (all data)	R1 = 0.0502, wR2 = 0.1129	
Extinction coefficient	0.0074(4)	
Largest diff. peak and hole	0.528 and -0.580 e.Å^-3	

Table 5-1b. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **17**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ge(1)	2983(1)	-132(1)	7563(1)	21(1)
Si(1)	1631(1)	544(1)	7565(1)	19(1)
Si(2)	2670(1)	1213(1)	8348(1)	21(1)
Si(3)	2386(1)	56(1)	8641(1)	19(1)
Si(4)	3033(1)	-1214(1)	6929(1)	28(1)
Si(5)	227(1)	650(1)	6775(1)	22(1)
Si(6)	2451(1)	2232(1)	8994(1)	22(1)
Si(7)	2108(1)	-491(1)	9704(1)	24(1)
C(1)	3903(1)	609(1)	7610(1)	22(1)
C(2)	3725(1)	1185(1)	7961(1)	23(1)
C(3)	1862(2)	-1568(1)	6814(2)	44(1)
C(4)	3293(2)	-1048(1)	5982(1)	34(1)
C(5)	2971(2)	-1672(1)	5490(1)	50(1)
C(6)	2764(2)	-413(1)	5660(1)	42(1)
C(7)	4292(2)	-928(1)	5988(1)	40(1)
C(8)	3833(2)	-1847(1)	7508(1)	37(1)
C(9)	3389(2)	-2086(1)	8133(2)	51(1)
C(10)	4006(2)	-2498(1)	7077(2)	54(1)
C(11)	4734(2)	-1512(1)	7822(1)	44(1)
C(12)	-90(2)	-240(1)	6402(1)	36(1)
C(13)	423(1)	1231(1)	5992(1)	27(1)
C(14)	-434(2)	1316(1)	5426(1)	42(1)
C(15)	1134(2)	886(1)	5627(1)	45(1)
C(16)	777(2)	1949(1)	6243(1)	38(1)
C(17)	-692(1)	946(1)	7283(1)	28(1)
C(18)	-1609(2)	969(2)	6800(2)	70(1)
C(19)	-515(2)	1661(2)	7618(2)	61(1)
C(20)	-741(2)	431(2)	7879(2)	86(1)
C(21)	1410(1)	2123(1)	9395(1)	31(1)
C(22)	2285(1)	3014(1)	8350(1)	30(1)
C(23)	1318(2)	2985(1)	7919(1)	39(1)
C(24)	2393(2)	3711(1)	8758(1)	39(1)
C(25)	2930(2)	2994(1)	7814(2)	46(1)
C(26)	3449(2)	2327(1)	9773(1)	34(1)
C(27)	3220(2)	2808(1)	10364(1)	51(1)
C(28)	4298(2)	2599(1)	9530(2)	48(1)
C(29)	3671(2)	1614(1)	10117(1)	44(1)
C(30)	1591(2)	208(1)	10187(1)	40(1)
C(31)	1231(2)	-1217(1)	9471(1)	33(1)
C(32)	400(2)	-909(1)	8998(2)	51(1)
C(33)	1558(2)	-1803(1)	9040(2)	76(1)
C(34)	954(2)	-1520(2)	10144(2)	74(1)
C(35)	3217(2)	-760(1)	10299(1)	35(1)
C(36)	3865(2)	-145(1)	10410(2)	50(1)
C(37)	3068(2)	-982(2)	11037(2)	80(1)
C(38)	3685(3)	-1342(2)	9964(2)	113(2)
C(39)	4666(1)	573(1)	7215(1)	23(1)
C(40)	5441(1)	193(1)	7462(1)	32(1)
C(41)	6130(2)	170(1)	7064(1)	45(1)
C(42)	6052(2)	517(2)	6422(1)	49(1)
C(43)	5286(2)	904(1)	6172(1)	44(1)
C(44)	4601(2)	929(1)	6568(1)	34(1)

Table 5-1c. Bond lengths [Å] and angles [deg] for **17**

Ge(1)-C(1)	1.9894(18)	Ge(1)-Si(3)	2.4076(5)	Ge(1)-Si(4)	2.4161(5)
Ge(1)-Si(1)	2.4309(5)	Si(1)-Si(2)	2.3429(7)	Si(1)-Si(3)	2.3435(7)
Si(1)-Si(5)	2.3754(7)	Si(2)-C(2)	1.8796(19)	Si(2)-Si(3)	2.3590(7)
Si(2)-Si(6)	2.3707(7)	Si(3)-Si(7)	2.3761(7)	Si(4)-C(3)	1.877(2)
Si(4)-C(8)	1.919(2)	Si(4)-C(4)	1.931(2)	Si(5)-C(12)	1.885(2)
Si(5)-C(17)	1.920(2)	Si(5)-C(13)	1.924(2)	Si(6)-C(21)	1.885(2)
Si(6)-C(26)	1.918(2)	Si(6)-C(22)	1.927(2)	Si(7)-C(30)	1.881(2)
Si(7)-C(35)	1.916(2)	Si(7)-C(31)	1.927(2)	C(1)-C(2)	1.348(2)
C(1)-C(39)	1.489(2)	C(4)-C(7)	1.530(3)	C(4)-C(6)	1.530(3)
C(4)-C(5)	1.546(3)	C(8)-C(11)	1.530(3)	C(8)-C(9)	1.535(3)
C(8)-C(10)	1.547(3)	C(13)-C(16)	1.530(3)	C(13)-C(15)	1.535(3)
C(13)-C(14)	1.534(3)	C(17)-C(20)	1.517(3)	C(17)-C(18)	1.517(3)
C(17)-C(19)	1.523(3)	C(22)-C(25)	1.533(3)	C(22)-C(23)	1.543(3)
C(22)-C(24)	1.545(3)	C(26)-C(29)	1.534(3)	C(26)-C(28)	1.537(3)
C(26)-C(27)	1.540(3)	C(31)-C(34)	1.528(3)	C(31)-C(32)	1.526(3)
C(31)-C(33)	1.530(4)	C(35)-C(37)	1.517(4)	C(35)-C(38)	1.526(4)
C(35)-C(36)	1.532(3)	C(39)-C(44)	1.391(3)	C(39)-C(40)	1.393(3)
C(40)-C(41)	1.395(3)	C(41)-C(42)	1.373(4)	C(42)-C(43)	1.389(4)
C(43)-C(44)	1.389(3)				
C(1)-Ge(1)-Si(3)	102.88(5)	C(1)-Ge(1)-Si(4)	123.93(5)	Si(3)-Ge(1)-Si(4)	127.04(2)
C(1)-Ge(1)-Si(1)	101.45(5)	Si(3)-Ge(1)-Si(1)	57.935(17)	Si(4)-Ge(1)-Si(1)	124.65(2)
Si(2)-Si(1)-Si(3)	60.45(2)	Si(2)-Si(1)-Si(5)	140.55(3)	Si(3)-Si(1)-Si(5)	145.11(3)
Si(2)-Si(1)-Ge(1)	80.09(2)	Si(3)-Si(1)-Ge(1)	60.534(17)	Si(5)-Si(1)-Ge(1)	134.70(2)
C(2)-Si(2)-Si(1)	105.02(6)	C(2)-Si(2)-Si(3)	105.65(6)	Si(1)-Si(2)-Si(3)	59.79(2)
C(2)-Si(2)-Si(6)	115.72(6)	Si(1)-Si(2)-Si(6)	129.95(3)	Si(3)-Si(2)-Si(6)	128.00(3)
Si(1)-Si(3)-Si(2)	59.76(2)	Si(1)-Si(3)-Si(7)	141.26(3)	Si(2)-Si(3)-Si(7)	133.47(3)
Si(1)-Si(3)-Ge(1)	61.530(17)	Si(2)-Si(3)-Ge(1)	80.250(19)	Si(7)-Si(3)-Ge(1)	143.39(3)
C(3)-Si(4)-C(8)	108.63(11)	C(3)-Si(4)-C(4)	107.65(11)	C(8)-Si(4)-C(4)	114.84(10)
C(3)-Si(4)-Ge(1)	104.86(8)	C(8)-Si(4)-Ge(1)	109.97(7)	C(4)-Si(4)-Ge(1)	110.37(7)
C(12)-Si(5)-C(17)	107.46(10)	C(12)-Si(5)-C(13)	107.97(10)	C(17)-Si(5)-C(13)	116.10(9)
C(12)-Si(5)-Si(1)	107.17(8)	C(17)-Si(5)-Si(1)	111.06(7)	C(13)-Si(5)-Si(1)	106.72(7)
C(21)-Si(6)-C(26)	107.55(10)	C(21)-Si(6)-C(22)	108.67(9)	C(26)-Si(6)-C(22)	113.82(10)
C(21)-Si(6)-Si(2)	108.73(7)	C(26)-Si(6)-Si(2)	108.12(7)	C(22)-Si(6)-Si(2)	109.82(7)
C(30)-Si(7)-C(35)	107.95(11)	C(30)-Si(7)-C(31)	107.50(11)	C(35)-Si(7)-C(31)	115.55(10)
C(30)-Si(7)-Si(3)	104.31(7)	C(35)-Si(7)-Si(3)	110.22(8)	C(31)-Si(7)-Si(3)	110.63(7)
C(2)-C(1)-C(39)	121.99(16)	C(2)-C(1)-Ge(1)	114.42(13)	C(39)-C(1)-Ge(1)	123.16(13)
C(1)-C(2)-Si(2)	118.53(14)	C(7)-C(4)-C(6)	109.1(2)	C(7)-C(4)-C(5)	109.04(18)
C(6)-C(4)-C(5)	107.41(19)	C(7)-C(4)-Si(4)	112.89(15)	C(6)-C(4)-Si(4)	108.68(14)
C(5)-C(4)-Si(4)	109.58(17)	C(11)-C(8)-C(9)	108.4(2)	C(11)-C(8)-C(10)	108.9(2)
C(9)-C(8)-C(10)	107.61(19)	C(11)-C(8)-Si(4)	112.25(15)	C(9)-C(8)-Si(4)	108.08(16)
C(10)-C(8)-Si(4)	111.51(17)	C(16)-C(13)-C(15)	107.29(19)	C(16)-C(13)-C(14)	108.90(17)
C(15)-C(13)-C(14)	107.84(18)	C(16)-C(13)-Si(5)	112.61(14)	C(15)-C(13)-Si(5)	108.28(14)
C(14)-C(13)-Si(5)	111.71(15)	C(20)-C(17)-C(18)	107.6(3)	C(20)-C(17)-C(19)	108.3(2)
C(18)-C(17)-C(19)	107.3(2)	C(20)-C(17)-Si(5)	108.40(15)	C(18)-C(17)-Si(5)	112.11(16)
C(19)-C(17)-Si(5)	112.97(14)	C(25)-C(22)-C(23)	107.9(2)	C(25)-C(22)-C(24)	109.35(18)
C(23)-C(22)-C(24)	107.42(17)	C(25)-C(22)-Si(6)	111.88(14)	C(23)-C(22)-Si(6)	107.91(14)
C(24)-C(22)-Si(6)	112.16(16)	C(29)-C(26)-C(28)	107.63(19)	C(29)-C(26)-C(27)	107.1(2)
C(28)-C(26)-C(27)	108.95(19)	C(29)-C(26)-Si(6)	108.67(14)	C(28)-C(26)-Si(6)	112.86(17)
C(27)-C(26)-Si(6)	111.39(16)	C(34)-C(31)-C(32)	108.4(2)	C(34)-C(31)-C(33)	109.1(2)
C(32)-C(31)-C(33)	106.8(2)	C(34)-C(31)-Si(7)	111.84(18)	C(32)-C(31)-Si(7)	108.17(15)
C(33)-C(31)-Si(7)	112.42(16)	C(37)-C(35)-C(38)	109.5(3)	C(37)-C(35)-C(36)	106.9(2)
C(38)-C(35)-C(36)	107.0(3)	C(37)-C(35)-Si(7)	110.8(2)	C(38)-C(35)-Si(7)	112.37(18)
C(36)-C(35)-Si(7)	110.02(15)	C(44)-C(39)-C(40)	118.31(18)	C(44)-C(39)-C(1)	118.87(17)
C(40)-C(39)-C(1)	122.82(18)	C(39)-C(40)-C(41)	120.4(2)	C(42)-C(41)-C(40)	120.7(2)
C(41)-C(42)-C(43)	119.6(2)	C(44)-C(43)-C(42)	119.8(2)	C(43)-C(44)-C(39)	121.3(2)

Symmetry transformations used to generate equivalent atoms:

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